

Appendix A



Phenolic Novolac And Resol Resins

The Plenco Difference



Phenolic thermosetting resin products are some of the most adaptive materials in the marketplace and hundreds of industries benefit from their use. Five generations of product designers worldwide have come to rely on phenolic-resin-based materials many times a day. Plastics Engineering Company is proud of our history designing materials that have passed the test of time, whether used in the morning coffee maker, the Apollo lunar module, or the newest automotive safety systems.

The market demands custom product development as resin applications become more specialized. The type of phenolic resin, its molecular weight, monomer and moisture content, viscosity or molten flow, pH, particle size, reactivity during cure, and cure vapor emission level are but some properties that determine our products' suitability for a customer.

The PLENCO phenolic resin team's mission is to develop, manufacture, and service useful products that provide clear value for our customers. Plastics Engineering Company's experience and ability to select product formulation options and to use a variety of manufacturing methods allow tailoring PLENCO resins to meet the requirements and expectations of our customers. We welcome the opportunity to customize a phenolic resin product for your application.

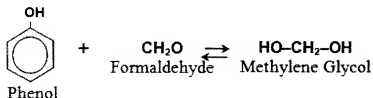
Plastics Engineering Company supplies modified and un-modified novolac and resol phenolic resin products as pastilles, powders, flakes, lumps, and solvent- or water-based liquids. In general, customers use PLENCO products to create impervious bonding matrices with fillers and substrates, to form protective coatings, to create rigid foams, as a source of amorphous carbon, or as chemically reactive additives.

What are Plenco Phenolic Resins?

Resins are polymers made by repeatedly linking discrete molecules (monomers) together to form chains or networks. PLENCO phenolic resins are oligomers (polymers with a few repeating units) synthesized by repeatedly linking phenolic (hydroxy-aromatic) monomers with aldehyde chemicals. The majority of PLENCO products are combinations of phenol (hydroxybenzene, C_6H_6O) and formaldehyde (methanal, CH_2O), though specialized applications may require use of substituted phenols (e.g., cresols, resorcinol, cashew nutshell liquid distillate), or other aldehydes (e.g., furfural). Phenolic resin manufacturers polymerize phenol by substituting formaldehyde on the phenol's aromatic ring via a condensation reaction. The selection of suitable reaction parameter results in optimum molecular weight distribution and residual monomer content necessary for maximum efficiency when used by the customer. The wide range of reaction conditions and monomers available to the resin producer allows for the production of a variety of resins specifically designed for use in individual applications.

We present the general chemistry of the polymerization of phenol with formaldehyde, the most common molecules used, to provide a general background of resin manufacture.

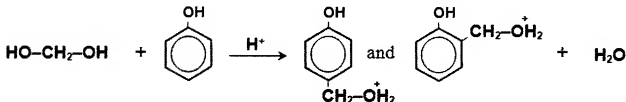
In aqueous solution, formaldehyde exists in equilibrium with methylene glycol.



Depending on the pH of the catalyst, these monomers react to form one of two general resin types: NOVOLAC RESINS and RESOL RESINS.

Novolac Resins

An acidic catalyst and a molar excess of phenol to formaldehyde are conditions used to make novolac resins. The following simplified chemistry illustrates the wide range of polymers possible. The initial reaction is between methylene glycol and phenol.



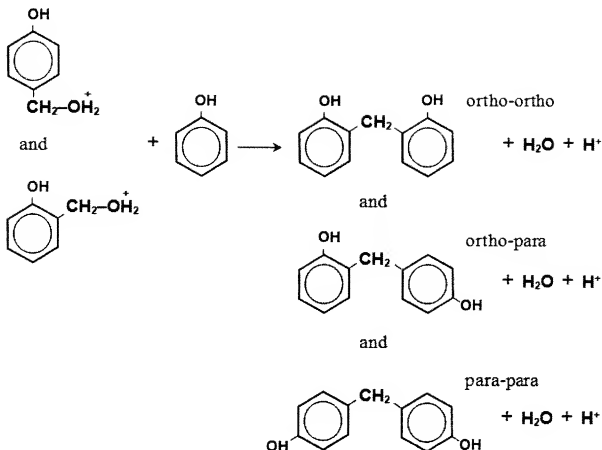
The reaction continues with additional phenol, and splitting off of water.

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The reaction creates a methylene bridge at either the ortho position or the para position of the phenolic aromatic rings. The “rule of thumb” is that the para position is approximately twice as reactive as the ortho position, but there are twice as many ortho sites (two per phenol molecule) so the fractions of ortho-ortho, para-para and ortho-para bridges are approximately equal.

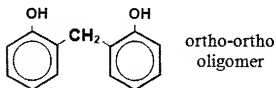
Branching occurs because reaction can occur at any of three sites on each ring. As the reaction continues, the random orientations and branching quickly result in an extremely complex mixture of polymers of different sizes and structures. The reaction stops when the formaldehyde reactant is exhausted, often leaving up to 10% of un-reacted phenol. Distillation of the molten resin during manufacturing removes the excess phenol and water.

The final novolac resin is unable to react further without the addition of a cross-linking agent. PLENCO novolac resins come with and without a curing agent. The resins having the curing agent incorporated cure or “thermoset” to the desired degree when processed by the customer.

Because an additional agent is required to complete the resin’s cure, the industry commonly refers to novolac resins as “two-stage” or “two-step” products. The most common phenolic resin cross-linking agent is hexamethylenetetramine, also known as hexa, hexamine, or HMTA. Ground and blended with the resin, hexa serves as a convenient source of formaldehyde when heated to molding and curing temperatures. A special attribute of hexa is that it reacts directly with resin and phenol without producing appreciable amounts of free formaldehyde. Hexa cures the resin by further linking and polymerizing the molecules to an

infusible state. Due to the bond angles and multiple reaction sites involved in the reaction chemistry, the resulting polymer is not a long straight chain but rather a complex three-dimensional polymer network of extreme molecular weight. This tightly cured bonding network of aromatic phenolics accounts for the cured materials' hardness, and heat and solvent resistant properties.

Certain catalysts can affect the orientations of the methylene linkages. Catalysts that preferably promote ortho-ortho linkages tend to preserve the more reactive para positions:



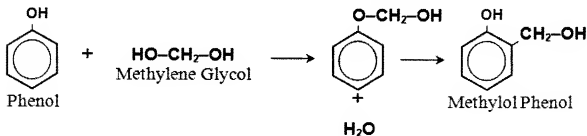
Novolac resins made with these catalysts tend to cure more rapidly than the standard randomly linked resins.

Novolac resins are amorphous (not crystalline) thermoplastics. As they are most typically used, they are solid at room temperature and will soften and flow between 150° and 220°F (65°C – 105°C). The number average molecular weight (Mn) of a standard phenol novolac resin is between 250 and 900. As the molecular weight of phenol is 94 grams per mole, a Mn of 500 corresponds to a resin where the average polymer size in the entire distribution of polymers is five linked phenol rings. Novolac resins are soluble in many polar organic solvents (e.g., alcohols, acetone), but not in water.

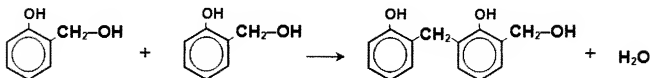
Resol Resins

A basic (alkaline) catalyst and, usually but not necessarily, a molar excess of formaldehyde is used to make resol resins. The following two stages describe a simplified view of the reaction:

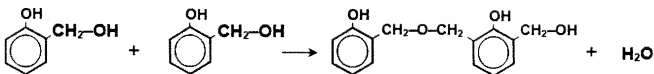
First, phenol reacts with methylene glycol to form methylol phenol:



Methylol phenol can react with itself to form a longer chain methylol phenolic:



or form dibenzyl ether:



or react with phenol to form a methylene bridge.



The most important point in resol resin chemistry is that, when an excess of formaldehyde is used, a sufficient number of methylol and dibenzyl ether groups remain reactive to complete the polymerization and cure the resin without incorporation of a cure agent such as hexa. For this reason, the industry commonly refers to resol resins as "single-stage" or "one-step" type products. Resol resin manufacture includes polymerizing to the desired extent, distilling off excess water and quenching or tempering the polymerization reaction by rapid cooling. Because resol resins continue the polymerization reaction at even ambient temperatures, albeit at much slower rates than during manufacturing, they demonstrate limited shelf lives dependent on the resin character, storage conditions and application.

By manipulating the phenolic to aldehyde monomer ratio, pH, catalyst type, reaction temperature, reaction time, and amount of distillation, a variety of resin structures demonstrating a wide range of properties are possible. The typical number average molecular weight (M_n) of a straight phenol resol resin is between 200 and 450. Plastics Engineering Company supplies resol resins as liquids or in solvents with viscosities from 50 to 50,000 cps, or as solids in the form of lumps, granules, or fine powders. Organic solvents and the amount of water or phenol monomer left in the resin control the viscosity of the liquid resin products. Resol resins are usually water-soluble to a certain degree.

Characteristics

Bonding Strength

The primary use of phenolic resin is as a bonding agent. Phenolic resin effortlessly penetrates and adheres to the structure of many organic and inorganic fillers and reinforcements, which makes it an ideal candidate for various end uses. A brief thermal exposure to complete the cross-linking or "thermoset" process results in attainment of final properties. The unique ability of phenolic resin to "wet out" and to cross-link throughout the fillers and reinforcements provides the means to engineer the desired mechanical, thermal, and chemically resistant properties.

Applications benefiting from the hardness, and heat and chemical resistance properties afforded phenolic resins include abrasive grinding wheels, friction linings, refractory products, and other molded parts used in high temperature or aggressive environments. For years, phenolic resin's exceptional compatibility with cellulose fillers has been used to great benefit for particleboard, plywood, hardboard, oriented strand board, substrates for melamine laminates and decking applications. Composites for demanding applications such as on oil platforms, missile components, and heat shields are produced using phenolic resins along with process technologies such as resin transfer molding (RTM), pultrusion, or filament winding.

Liquid phenolic resins penetrate and saturate paper and other substrates to provide good mechanical strength, electrical properties, or filtration capabilities. Typical examples of these applications include NEMA electrical laminates, decorative laminates, clutch and transmission papers, and filtration products.

High Temperature Performance

A key characteristic of thermoset phenolic resin is its ability to withstand high temperature under mechanical load with minimal deformation or creep. In other words, cured phenolic resin provides the rigidity necessary to maintain structural integrity and dimensional stability even under severe conditions. For this reason, phenolic resin binders meet the challenges of high temperature environments in demanding applications such as refractory, friction, foundry and aerospace products. Examples of applications that take special advantage of the dimensional stability of phenolic molding compounds are natural gas valves, automotive brake pistons, pulleys, and hydraulic and water pump housings and seals.

Chemical Resistance

Phenolic resins accommodate the harsh exposure of severe chemical environments. The inherent nature of phenolic resin provides an impervious shield to protect a variety of substrates from the corrosive effects of chemicals. Laboratory tests confirm minimal degradation from many chemicals after prolonged exposure, often at elevated temperatures.

Typical exposures include gasoline, alcohol, oil, glycol, brake fluid, various hydrocarbons, and also weak acids and bases. Protective linings inside tankers used for bulk transfer of acids and other corrosive chemical products are often composed of phenolic resins.

Low Smoke and Toxicity

Burning phenolic resin typically generates hydrogen, hydrocarbons, water vapor, and carbon dioxide. Phenolic resin produces a relatively low amount of smoke at a relatively low level of toxicity. Manufacturers use phenolic resins extensively to address the safety concerns of the transportation industry. Automotive and mass transit industries choose phenolic resin for its high heat resistance and excellent flame, smoke, and toxicity properties. Another critical application is in air support systems for the mining industry and related electrical conduit supports. Phenolic resins designed to meet specific flammability ratings are available. Selective use of inorganic fillers and reinforcements often enhances protection in the event of contact with an ignition source.

High Carbon and Char Yield

Phenolic resins demonstrate higher char yields than other plastic materials when exposed to temperatures above their point of decomposition. In an inert atmosphere at high temperatures (600° - 2,000°F, 300 - 1,000°C), phenolic resin will convert to a structural carbon known as vitreous carbon. In many ways, this material behaves similar to ceramic and may actually contribute to structural integrity when exposed to fire situations. Manufacturers of structural composite gratings and pipes for offshore oilrigs, where fires are a constant threat, utilize phenolic resins for the characteristic. Phenolic resin is also useful in designing vitreous carbon articles such as special analytical electrodes, crucibles for melting rare earth metals, rocket nozzles, extremely high temperature bearings and seals, and heat shields for missiles. Automotive applications that benefit from the formation of a thin carbonized layer, such as brake blocks and pads, brake linings, and clutch facings also use phenolic resins.

The aerospace, defense, and electrical industries are heavily reliant on phenolic resins. Phenolic resin advantages include high heat resistance, excellent dimensional stability, as well as having a United Laboratories rating. Phenolic molding compound applications within these industries include electrical commutators, switches, business equipment, and wiring devices. Phenolic resin retains its strength at high temperatures, resists creep under load, and possesses chemical and corrosive resistance. Phenolic resins are widely incorporated in household appliances because of their excellent electrical resistance, dimensional and thermal stability, and resistance to water and solvents.

Applications - Examples

Ablation

Phenolic resin chars when heated to temperatures greater than 480°F (250°C). This process continues at very high temperatures greater than 1,000°F (>500°C), until the resin completely converts to amorphous carbon. This characteristic contributes to the unique ablative properties of phenolic resins. An ablative surface is a heat shield designed to wear away in a controlled fashion at very high temperatures. Examples are rocket nozzles, rocket blast shields, and atmospheric reentry shields.

Several aerospace ablative applications specify PLENCO resins.

Abrasives

The variety of abrasive products available in the market is practically endless, as they have to meet the specific needs of the individual grinding applications and substrates. Applications range from simple cut off wheels to precision sanding tasks, and involve materials like metal, wood, minerals, and composites. Generally, there are three groups of abrasive products: bonded, coated, and non-woven.

Bonded abrasives

Bonded abrasives like grinding wheels are comprised of abrasive particles embedded in a bonding matrix. While the grit used may be from a wide variety of minerals and abrasive particles, phenolic resin is the matrix binder of choice. Achieving the optimal combination of resistance to burst or fracture strength, flexibility and porosity, coupled to the manufacturing method, requires optimization of the binding resin to the specific application of the wheel in question. Modification of the blend of phenolic novolac powder, hexa, and liquid resol resin is usually needed to achieve such optimization. For increased strength, fiberglass reinforcement inlays are used. These inlays are themselves typically saturated with a special liquid phenolic

resin.

Plastics Engineering Company tailors powdered and liquid resins for bonded abrasives to the specific needs of the customers and their unique cold forming or hot molding process. Accelerated cure resins are available as well as dust reduced powdered novolac-hexa products. PLENCO resins are available as solvent-based flexible phenolic resins for use in fiberglass reinforcement inlays as well.

Coated Abrasives

Coated abrasives are flexible grinding materials typically available as sheets, discs or belts. These applications require abrasive grains fixed to the surface of a variety of backings, like paper or fabric, by special liquid phenolic resin binders. The manufacture of coated abrasives with their unique properties requires multiple production steps.

PLENCO resins in solvent or aqueous liquid solutions meet the special requirements of this application.

Non-Woven Abrasives

Household and industrial applications use non-woven abrasives, also called abrasive pads. The characteristically green pads used for cleaning the dishes are the most publicly visible non-woven abrasive.

Manufacturers of non-woven abrasive parts typically employ the use of liquid phenolic binders.

PLENCO phenolic resins provide the excellent wetting properties and the short drying times needed by abrasive pad manufacturers to meet the technical requirements while achieving a high line speed for improved productivity.

Adhesives

Wood bonding applications such as particleboard or wafer-board have traditionally used phenolic resin binders. Due to their specific "affinity" for wood and wood fibers, special liquid phenolic resins may be required for the specialty wood adhesives industry typically in combination with a polyvinylacetate (PVAc) backbone polymer.

PLENCO liquid phenolic resol resins with low free phenol and low free formaldehyde contents are available especially for use in adhesive applications. Plastics Engineering Company can also supply low ash content, soluble solid resol resins, and of course a wide range of novolac resin-hexa systems.

Carbon

Phenolic resins have an excellent affinity for graphitic and other forms of carbon. Manufacturers often use the resin simply as a binder and adhesive for their carbon materials. At high temperature, phenolic resins form a char of amorphous carbon. This means phenolic bonded carbon materials can be heat treated to yield an all carbon structure. Because of these unique properties, phenolic resins find application in the manufacture of electrodes, carbon-carbon composites, carbon seals, and washers.

Phenolic resins are the binder of choice for manufacturing the carbon brushes used in electrical motors, starters and the like. Depending on the manufacturing process, powdered or

liquid solutions of novolac resin-hexa blends, powdered resol resins, and liquid resol binding systems provide the desired binding properties.

Several PLENCO phenolic resins meet the requirements demanded by this technically challenging application.

Coatings

Cured phenolic resins demonstrate exceptional chemical resistance. Railroad cars, storage tanks and heat transfer equipment are coated using phenolic resins as part of baked phenolic coating systems.

PLENCO straight phenolic resin systems approved for coating applications are available and the researchers at Plastics Engineering Company are ready to tailor a resin system to the requirements of the customer.

Composites

Phenolic resins are the polymer matrix of choice in composite products especially when meeting high flame, smoke and toxicity (FST) properties. Phenolic resins provide for excellent strength at elevated temperatures in a variety of environments and are compatible with a multitude of composite fibers and fillers. Multiple applications benefit by using phenolic resins in the following composite part manufacturing processes:

- Resin Transfer Molding
- Pultrusion and Profile Extrusion
- Filament Winding
- Hand Lay-up

Lightweight and high strength honeycomb structured core materials for aircraft and other aerospace applications utilize phenolic binding resins, usually in a dipping-saturating process.

The composite manufacturing processes and components vary significantly from product to product and process to process so that customized PLENCO phenolic resins are the best answer for our customers to find the optimum process and composite performance.

Felt Bonding

Fiber felt manufacturers use phenolic resins with reclaimed or virgin fibers to produce thermal and acoustical insulation for the automotive and household appliance industries. Felt manufacturers achieve optimum rigidity, sound absorption and acoustical insulation performance by varying the density of the felt product. The versatility of the phenolic resin to affect the part density mirrors the versatility of substrate fibers used. Phenolic resins provide exceptional resistance under all environmental conditions.

Specific applications are:

- Functional components used in visible areas (e.g., package deck)
- Below surface products used for padding and sound absorption (e.g., hood liner)
- Rigid parts used as substrate for decorative material

Felt manufacturers achieve specific performance requirements by judicious use of PLENCO powder resins. Resin formulation provides for good mold release, improved compatibility with scrim materials, and accelerated cure speeds for production efficiency.

Environmental considerations continue to grow in importance. PLENCO phenolic resins for felt bonding applications exhibit low emission and odor levels. Low dust level versions of PLENCO phenolic resins are available also.

Foam

Special phenolic resins in combination with the proper cure catalysts, surfactants and blowing agents produce foam products. Phenolic foam has a unique set of properties such as excellent fire and heat resistance and a low smoke and toxicity rating when burned. Proper surfactants produce closed cell foams with excellent insulating R-values. Other surfactants produce open cell foams demonstrating unique water absorption properties.

Typical application fields are:

- Floral foam (dry and wet foams)
- Orthopedic foam (for making foot print casts)
- Insulating Foams

PLENCO phenolic resins are widely accepted by the foam industry for their superior consistency, crucial for the challenging production process.

Foundry

Many technologies are available to foundries for the production of dies for metal castings. Manufacturers using the shell molding process experience excellent dimensional accuracy, surface smoothness and high production rates using phenolic resin coated foundry sands. The shell molding process involves first creating mold cavities and cores by shaping sand coated with phenolic resin over a not metal form. Removed from the form and assembled, the mold and cores create the "negative" shape of the desired metal form. Hot metal is poured into the resin-sand mold and allowed to cool. Once hard, the excess resin-sand material is broken away revealing the metal part. Some recover the broken away sand for reuse. The careful selection of sand type, resin characteristics and coating method results in the desired mold and core properties such as strength, rigidity, flexibility, surface finish, part release and applicability to reuse.

Plastics Engineering Company provides phenolic novolac sand coating resins in pastille form, for consistent melting and coating, efficient transport, and low dust. Resin formulations make use of proprietary accelerants, plasticizers or release agents to achieve a wide range of properties. These additives together with a customized phenol level, melt point, and hexa amount achieve optimal performance for each foundry's requirements, like a low peel to improve release from the hot metal former. The PLENCO product range includes resins for core sands, mold sands, and recyclable sand.

Friction

Phenolic thermoset resin is the choice for composite friction materials: the pads, blocks, linings, discs and adhesives used in brake & clutch systems that create retarding or holding

forces with application against a moving part. The inherently heat resistant phenolic resin carbonizes and chars at extreme service temperatures, it does not melt and smear like other polymer matrices. This property results in restored friction properties when the material cools and "recovers" from hard braking.

Formulas for phenolic composite friction materials are combinations of friction and wear-controlling agents, reinforcing fibers and inert fillers blended with un-cured phenolic resin in an amount necessary to bond the other ingredients in place with sufficient strength and resiliency when finished. Judicious selection of the types and amounts of raw materials used allows for the optimization of performance with cost and consistency. Formulas for basic friction applications may contain 5 to 10 different ingredients while specialized material formulas may include a score or two of raw materials. Only one type of bonding resin is typically used. The effect of that one binder on the final composite's properties depends on the total formulation and manufacturing method however. That is, no single type of resin product works optimally with all friction formulas or applications.

The salient step in the manufacture of phenolic composite friction materials is the molding and initial curing of the composite under heat and pressure. This molding step typically involves pressing a uniform blend of ingredients in a shaped mold preheated to 280° - 400°F (140° - 200°C) from one to three tons of pressure per square inch. The phenolic resin melts and flows during the molding operation to coat and then secure the other ingredients when the resin cross-links or "cures" to an infusible state. The resin's performance during the hot molding step is most important to assuring an efficient manufacturing process. Friction material manufacturers select the type and amount of binder resin product used as a complement to the envisioned manufacturing process, its compatibility with other raw materials, environmental concerns and the expected service requirements.

To this end, Plastics Engineering Company is uniquely suited to assist friction material designers with a number of liquid and solid novolac (2-stage) and resol (1-stage) phenolic resins demonstrating a wide variety of flow and cure character combinations. The resins can be custom formulated with cure accelerating or performance enhancing additives. PLENCO resins are suitable for all types of brake and clutch uses, including pads for lawn & garden equipment and automotive brakes, blocks for on and off road trucks, and linings for industrial, oil field and marine friction applications.

Proppants (Frac Sand)

Oil and natural gas producers improve well yields using hydraulic fracturing fluids containing round specialty sands coated with phenolic resin. The industry refers to these sands as proppant or frac sands.

The hydraulic fracturing fluid containing the proppant sand is pumped into the well effectively pressurizing the borehole and fracturing the surrounding rock. The fluid fills the nascent fissures and the resin-coated sand works as a prop to keep the fissure from sealing on release of pressure. Round sand is used to provide a porous medium through which the oil and gas can easily flow.

Proprietary proppant sands made with PLENCO resins continually improve petroleum yields every day.

Refractory

High carbon yield, wear resistance, and excellent particle wetting and bonding properties make phenolic resins ideal for refractory products. There are two general categories of refractory products: shaped and unshaped. Hydraulically pressed refractory bricks, slide gates, shrouds, nozzles, and crucibles are examples of shaped products. Examples of unshaped products are tap-hole compounds, tundish liners and ramming mixes used in steel making. Plastics Engineering Company provides phenolic refractory resins as liquids in a variety of solvents, including water based systems. Manufacturers may also choose from a wide range of novolac-hexa powder resin products.

Some companies combine phenolic resins with temperature resistant ceramic fibers in a vacuum forming process to manufacture riser sleeves, ladles, and hot toppings. This application typically uses novolac-hexa powder resins with low emission levels. Non-hexa cured PLENCO resins are available for this application to reduce ammonia and formaldehyde emissions.

Rubber

Tires and technical rubber goods use straight phenolic novolac resins as reinforcing agents. PLENCO novolac resin pastilles are the preferred choice for a manufacturer who compounds the resin into the rubber for superior mix consistency and reduced dusting when compared to using powders or resin in flaked form. Special effort assures consistent pastille size and shape to meet the requirements of the automated dosing systems used by the industry. PLENCO phenolic novolac pastille resins are available in a variety of softening point and emission level versions.

Some rubber applications require phenolic novolac-hexa powder resin products in combination with the rubber compound. Plastics Engineering Company provides novolac-hexa with customized flow and the hexa curing agent level specific to each application.

Substrate Saturation

Many applications use liquid phenolic resins to saturate substrates such as paper, fabrics, and wood. Phenolic resins receive preference because of their high mechanical strength, outstanding chemical resistance, and good flame resistant properties. Typically, solvent-borne resol resins are used, but depending on the specific products and processes, aqueous resol resins or resol cured novolac resins in solvents are preferred.

Typical application fields are:

- Paper laminates (decorative or functional)
- Engineered wood
- Filter paper impregnation (Oil filters, Gasoline filters, Air filters)

Plastics Engineering Company provides resins for the full range of technologies used in this application field and works to customize specific phenolic resins to the requirements of the individual customer.

CHARACTERIZATION OF A NOVOLAC RESIN SUBSTITUTING PHENOL BY AMMONIUM LIGNOSULFONATE AS FILLER OR EXTENDER

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In this work two types of lignin-novolac resins have been formulated, partially substituting phenol by softwood ammonium lignosulfonate as filler or extender (methylolated) to study the viability of that substitution when resins will be employed as adhesives in textile felts. A commercial novolac resin was used as reference. Free phenol, free formaldehyde, water content, softening point, and flow distance values were determined in all cases to verify whether the material fulfills specifications. In addition, FTIR and NMR spectroscopic techniques were employed for the characterization of three resins samples tested to discuss their structural differences and similarities. The results obtained have shown that the substitution proposed is feasible from the point of view of the resins synthesis to get the pre-polymer.

Keywords: Phenolic Resins, Ammonium Lignosulfonate, Methylolation, Synthesis

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INTRODUCTION

There are two types of phenolic resins: resol and novolac. The first one is synthesized under basic pH conditions with excess of formaldehyde, and the latter is carried out at acidic pH (with an excess of phenol). They are widely used in industry because of their chemical resistance, electrical insulation, and dimensional stability (Gardziella et al. 2000). There are some published works involving lignin-resol resins (Kou et al. 1991; Vázquez et al. 1997; Danielson et al. 1998; Alonso et al. 2001), fewer employing lignin-novolac for different applications (El-Saied et al. 1984; Ysbrandy et al. 1992), but there has not been any work involving lignin-novolac combinations for textile-felts applications, which is the focus of the present paper. Phenolic resin-bonded textile felts can be considered to be fiber-reinforced plastic with a high level of fibers. These fibers are derived from textile scraps recycled from the textile industry.

Due to the increase of phenol cost, researchers have been working to partially substitute this monomer by natural polymers that present similar structure in the resin without modification of resin properties (Gardziella et al. 2000). One of these possible substitutes, among other natural compounds, is lignin, a polydisperse natural polymer constituted mainly of phenyl propane units, which present a structure close to that of phenolic resin (Forss et al. 1979).

Lignin is a by-product of the pulp and paper industry that can be present in many different forms. The choice of the type of lignin to incorporate into resin synthesis has been based on cost and availability (Alonso et al. 2001). The kraft process consumes most of the lignin in the process of recovering the reagents used in pulping. Organosolv lignins are not available in great amounts. So, the best possible substitutes of phenol by lignin-derived chemicals at an industrial scale are the lignosulfonates, which are obtained from the sulphite process. Among the different types of lignosulfonate, the ammonium lignosulfonate is the most suitable to substitute phenol, because final properties of phenolic resins are better (Calvé et al. 1988; Allan et al. 1989). In a previous work it has been verified that the lignosulfonate that better adapts as copolymer in the formulation of resol type phenolic resins was the ammonic type from coniferous wood (Alonso et al. 2001). The results of that study make it possible to deduce that this type of lignin also can be useful for novolac resins. In addition, ammonium ion is used as an intermediate in the first stage of the curing reaction of the formulated resin, which favors this process (Zhang et al. 1997).

Lignosulfonates are not very reactive with phenol and formaldehyde; hence it is also usual to modify their structure. The most common ways of lignin modification are methylation (Dolenko et al. 1978; Peng et al. 1994; Alonso et al. 2001) and phenolation (Nada et al. 1987; Alonso et al. 2005). Both processes are able to activate lignin, but phenolation is less studied because of the high cost of this process. On the other hand, methylation does not need an expensive installation.

Novolac oligomers are prepared in acidic media, using an excess of phenol over formaldehyde. The mechanism associated with this reaction can be described in four steps. First, a methylene glycol is protonated by an acid from the reaction medium, which then releases water to form a hydroxymethylene carbonium ion. This ion acts as a hydroxyalkylating agent by reacting with phenol via electrophilic aromatic substitution. A pair of electrons from the benzene ring attacks the electrophile, forming a carbocation intermediate, followed by deprotonation and a regain of aromaticity. The methylol group of the hydroxymethylated phenol is unstable under acidic conditions and loses water readily to form a benzylic carbonium ion. This ion then reacts with another phenol to form a methylene bridge in another electrophilic aromatic substitution in the *ortho* and *para* positions. This major process repeats itself until the formaldehyde is exhausted (Knop and Pilato 1985). These pre-polymers are thermally stable and can be stored effectively. Novolac crosslinking is usually achieved by introducing a source of methylene groups to form additional methylene bridges between aromatic rings. Hexamethylenetetramine (HMTA) is the most widely used curing agent (source of formaldehyde) for these reactions.

The reaction mechanism associated with the formulation of lignin-novolac is similar to that of the conventional approaches previously described. Considering the particular case of the lignosulfonates employed in this work, the α -carbon of the lateral chain of the phenyl-propane units is occupied by the sulfonate group. Lignosulfonates may be reacting by itself or with phenol adding to the β -carbon of the lateral chain. The proposed mechanism for the reaction among the lignosulfonate with phenol and formaldehyde in acid medium is exhibited in Fig. 1 (Dos Santos, 1996). The first step consists of the condensation between lignin fragments and the phenol present with

formaldehyde. After that, in a second step, vacuum distillation is employed to adjust the content of free phenol in accordance with the required specifications for textile felt applications. The addition of a curing agent (HMTA) with methylene groups is also necessary for the crosslinking.

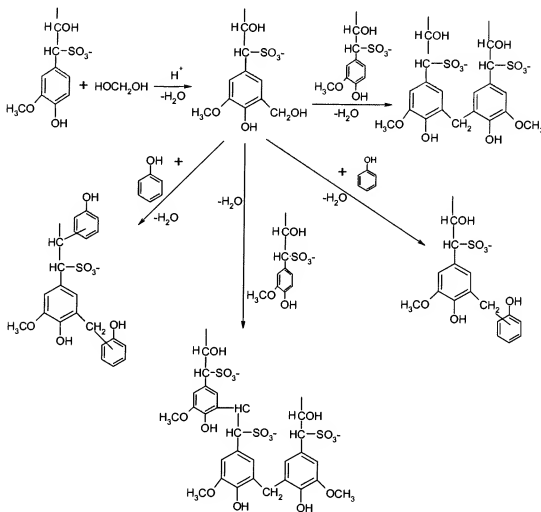


Figure 1. Mechanism of lignin-novolac resins synthesis substituted with lignosulfonates

In this work, two types of lignin-novolac resins were synthesized in the laboratory and compared with a commercial novolac. One lignin-novolac resin was formulated incorporating softwood ammonium lignosulfonate directly, as filler, and the other one incorporated ammonium lignosulfonate modified by methylation. Formulated resins were characterized in terms of free phenol, free formaldehyde and water contents, softening point, and flow distance to compare with properties of commercial resin. The structural differences among resins were established spectroscopically by Fourier Transform Infra-Red (FTIR) spectroscopy and ¹H and ¹³C Nuclear Magnetic Resonance

(NMR) techniques. The aim of this work was to study whether the partial substitution of phenol by lignin is feasible, attending to their chemical structure and the specifications for the final applications.

EXPERIMENTAL

Materials

Commercial novolac resin and hexamethylenetetramine were supplied by Hexion Speciality Chemicals Ibérica, S.A. The softwood ammonium lignosulfonate used was supplied by Borregaard Deutschland as Borrespense AM 320. This product resembles a spray-dried powder containing 80 wt% of lignosulfonate, 6% of ash, 4.22% of moisture, and 1.93% of phenolic hydroxyl groups. Lignin-novolac resins were synthesized by using commercial grades of phenol, formaldehyde, and oxalic acid.

Procedure

A commercial novolac resin (PF) was tested in this study as reference material. This product is obtained by the polymerization between formaldehyde and phenol in acidic medium. Lignin-novolac (LN) was formulated in the laboratory, substituting phenol by lignosulfonate at the beginning of the pre-polymer synthesis (Fig. 1). Methylolated lignin-novolac (MLN) resin was synthesized under the same operating conditions as LN resin, but using lignosulfonate modified by methylation. The details of this modification were reported in a previous article (Alonso et al. 2001). The substitution of phenol by ammonium lignosulfonate has been 30 wt% in both samples, because of higher amounts do not produce suitable resins (Ysbrandy et al. 1992; Kharade et al. 1998). The phenol/lignosulfonate (P/L) and phenol- lignosulfonate/formaldehyde (PL/F) molar ratios were 1/0.27 and 1/0.76, respectively.

The resins syntheses (LN and MLN) were carried out in a laboratory glass reactor (2 l) equipped with a stirrer, thermometer, and reflux condenser (Fig. 2.a), and were accomplished in four stages. First was the addition step, where lignosulfonate (modified or non-modified), phenol, and oxalic acid (0.5 wt% in relation to phenol) were dissolved and heated up to a temperature of 100 °C. Then, the formaldehyde (37 wt%) was added, with heating continued during 90 min. Second, the condensation reaction took place for 90 min (Fig. 2.a.). After the second stage, the installation was changed by a distillation system, as shown in Fig. 2.b. The water was removed by atmospheric pressure distillation followed by vacuum distillation to remove most of phenol and water. Finally, the resin was washed with distilled water to remove the phenol and achieve the required specifications.

Pre-Polymers Analysis

The parameters analyzed in the formulated samples were free phenol, free formaldehyde, water content, softening point, and flow distance. The values for these parameters must be in agreement with commercial resin specifications.

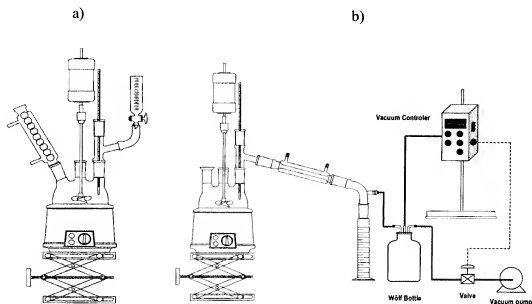


Figure 2. Scheme of experimental set-up of resins synthesis. a) Formaldehyde addition and reaction condensation; b) Atmospheric and vacuum distillations

Free phenol (P_f) was determined by gas chromatography, using a Varian 3400 chromatograph with a flame ionization detector (FID) and helium as carrier gas. An HP-INNOWax (crosslinked polyethylene glycol) high-performance capillary column of 0.2 μm film thickness, 50 m length, and 0.2 mm internal diameter was used. The internal standard employed was *p*-cresol, which was added to the methanol dissolved samples.

Free formaldehyde (F_f) was analyzed by the hydroxylamine hydrochloride method with endpoint titration (ISO 9397) by using a METTLER TOLEDO titrator DL-50. Free formaldehyde was also analyzed in the methylolated liginosulfonate in order to determinate its conversion in the reaction and formulation of prepolymer.

The resin or methylolated liginosulfonate (1 g) was dissolved in 60 mL of an isopropanol–water mixture (2:1, v/v); hydrochloric acid was added until the pH was between 2 and 3. Then, 0.1 N sodium hydroxide was used to adjust the pH to 3.5. Finally, 10 mL of the 10% hydroxylamine–hydrochloride solution was added. After 10 min, the solution was retitrated with 0.1 N sodium hydroxide up to pH = 3.5.

Water content (W_f) was determined according to DIN 51 777.1 and DIN 53 715 by using a Karl-Fischer Titrator (DL-31 Mettler-Toledo).

Softening point (SP) was performed in a Mettler-Toledo FP-900 with a FP83 measurement cell according to DIN 51920.

Flow distance (FD). From the powdered resin (mixture of sample novolac resin and 11 wt% HMTA), a tablet was formed. This tablet was placed on a pre-heated horizontal glass plate at 125 °C in an oven (ISO 8619). After 3 min, the plate was tilted to an angle of 60°. The flow distance was measured after 30 min and given in mm.

FTIR/NMR Spectroscopy

The commercial novolac, lignin-novolac, and methylolated lignin-novolac resins were characterized by FTIR and ^1H and ^{13}C NMR spectroscopic techniques in order to analyze the structural differences. In addition, the lignosulfonates (modified and without modifying) employed were also analyzed by using these techniques.

FTIR spectra were recorded with a Mattson Satellite spectrophotometer, using the potassium bromide pellet method. The pellet was prepared from a mixture of 300 mg potassium bromide and 5 mg of resin sample (or lignosulfonate). The operating conditions were: 4000-400 cm^{-1} spectral width, 32 accumulations, 1 gain, 4 cm^{-1} resolution, and signal processing by triangular apodization. Band assignments were based on cited studies (Morterra et al. 1985; Costa et al. 1997; Nada et al. 1998; Carotenuto et al. 1999; Sun et al. 2001).

^1H and ^{13}C NMR spectroscopy. The ^1H spectra were recorded on a 200 MHz NMR spectrometer (BRUKER AC 200). The conditions used were: 4000.000 Hz sweep width, 7.2 μs pulse width, and a temperature of 297 K. Samples (0.1 g) and 10 μL of tetramethylsilane (TMS) were dissolved in 1 ml of deuterated-dimethylsulfoxide (DMSO_{d6}). ^1H chemical shifts were measured with respect to TMS as internal standard ($\{\text{DMSO}_{d6}\} = 2.5 \text{ ppm}$). ^{13}C spectra were recorded on a 500 MHz NMR spectrometer (BRUKER AMX 500). In this case, the conditions used were: 90° pulse width, 6 s pulse time, 323 K, and 26000 sweeps. Peaks assessments were based on cited literature (Lundquist et al. 1989; Faix et al. 1994; Gardziella et al. 2000; Sun et al. 2001; Wang et al. 2005).

RESULTS AND DISCUSSION

Characterization of Novolacs

The required specifications for commercial (PF) resins and the results obtained in the characterization of lignin-novolac (LN) and methylolated lignin-novolac (MLN) are shown in Table 1. The free formaldehyde amounts of different samples fulfilled the specifications because these polymers are formulated with formaldehyde by default. In relation to free phenol content, lignin-resin (LN), and methylolated lignin resin (MLN) also conformed to the required values according to commercial resins specifications. Note that the methylolated lignin-novolac showed a free phenol content superior to that of the lignin-novolac resin. Methylolated lignin resin reduces the permeability in relation to LN and commercial resins, and therefore the pre-polymer offers resistance to the removal of phenol during the formulation.

Water content is also an important specification in the final application of these resins because it has a remarkable influence on the plasticity of novolacs. The effect on the melt viscosity is even more pronounced. For example, a buildup of the water content from 0.1 to 3% reduces the melt viscosity up to 90% (Knop and Pilato 1985). The reactivity of novolac to HMTA increases when water content increases, and the flow distance is reduced in spite of decreasing melt viscosity (Gardziella et al. 2000). The influence of free phenol is similar to water content but is less severe.

Table 1. Lignin-Resin Characteristics and Commercial Resin Specifications.

Resin	P _f (%)	F _f (%)	W _f (%)	SP (°C)	FD (mm)
LN	0.14	0.19	0.23	119	27
MLN	0.19	0.02	0.28	118	26
Commercial*	< 0.20	< 0.30	< 0.40	115-125	25-40

P_f: Free phenol; F_f: Free formaldehyde; W_f: Water content; SP: Softening point; FD: Flow distance. * Required specifications supplied by Hexion Ibérica, S.A.

In addition, curing reaction of novolacs is carried out over 100 °C, water forms vapor, and so the final material can present a porous structure with reduced mechanical properties. Therefore, a resin with low initial water content will achieve better final properties after curing. Note that all resins studied had less water than the maximum commercial specification, and lignin-novolac had less water than MLN because less water was used during formulation of LN resin (Table 1).

The softening point is a critical parameter in order to determine the feasibility of resins in textile-felt applications. If the softening point of lignin-resins is not in the commercial resin range (115-125 °C), then these pre-polymers would not be employed for textile-felts, because the resin could not penetrate into the fibers. In this case, the softening point temperatures of synthesized resins with ammonium lignosulfonate were in the specified range, as shown in Table 1.

Lignin-novolac and methylolated lignin-novolac resins had a flow distance within the commercial range, but these results were near the lower limit. This fact is due to the presence of lignin in the samples, which reduced chain mobility of the resins. In short, these two lignin-resins fulfilled the specifications required by the textile-felts manufacture.

The FTIR spectra of lignin-novolac, methylolated lignin-novolac, and commercial resins are shown in Fig. 3. The highest wavenumber zone did not offer any difference among the three resins assayed. However, the spectra showed more information about resins structure within the 2000 to 400 cm⁻¹ zone. The broad absorbance at 1701-1692 cm⁻¹ corresponding to C=O stretching was observed in MLN spectra, but not in the commercial spectrum (Faix et al. 1994; Nada et al. 1998). The most typical band of lignin structures is 1600 cm⁻¹. In this case, it was not present in commercial resin, but a 1610 cm⁻¹ band was able to overlap it. In addition, the 1470-1460 cm⁻¹ band was not very intensive, which indicates that methylolated lignin molecule incorporates hydroxymethyl groups in the MLN resin (Nada et al. 1998; Alonso et al. 2001). The main objective of methylation was to incorporate hydroxymethyl groups into the lignin aromatic ring. Note that LN resin also showed the same band (1470-1460 cm⁻¹), which implies that even without methylation this group can be incorporated into the aromatic ring of lignin. In addition, this band (1470-1460 cm⁻¹) overlapped with a 1430 cm⁻¹ band (methylene bridge), which is typical of novolac resins and in this case is not well resolved (Costa et al. 1997). The 819 cm⁻¹ band corresponds to out-of-plane aromatic ring deformation by 1, 2, and 4 links. The band at 754 cm⁻¹ is the 1, 2, and 6 substitutions of this aromatic ring. These two bands are quite similar in all resins due to great similarity of the substitutions,

as shown in Fig. 3. On the other hand, lignin-novolac and methylolated lignin-novolac had a predominance of 1, 2, and 6 links. This means that lignin aromatic rings have steric hindrance (Šebenić et al. 1974; Costa et al. 1997). The 655 cm^{-1} band in LN and MLN resins spectra indicates the presence of sulfonic groups from liginosulfonate.

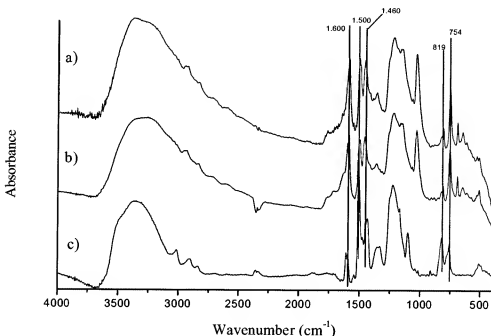


Figure 3. FTIR spectra of a) LN, b) MLN and c) Commercial novolac resins

The three resins studied also showed important differences in ^1H NMR spectra (Fig. 4). For instance, the 9 ppm zone corresponds to aldehyde protons linked to aromatic ring substitutions of the type $-\text{CHO}$. This signal did not appear in MLN, which implies that in this pre-polymer there were higher levels of substitutions than in the others resins. In addition, it supposes more steric hindrance to $-\text{CHO}$ group incorporation into the MLN aromatic rings. Signals corresponding to aromatic protons (6.5-7.0 ppm) showed the presence of more free positions in the aromatic rings of resins. An absence of signals in the range of 7.0 to 7.5 ppm for commercial resin spectrum showed that the aromatic rings were less substituted. The lignin-novolac and methylolated lignin-novolac resins exhibited a higher level of replacement at the aromatic ring, which indicates that crosslinking reactions will be favored during the curing stage. In lignin-novolac resins the decrease of protons signal of hydroxymethyl groups coming from lignin (4.5-4.6 ppm) demonstrated the dehydration of these groups to form methylene links with phenyl groups; this dehydration did not happen in commercial resins, which explain higher reactivity of lignin-novolac with the phenol. Thus, these circumstances are desirable for

resin-curing reactions. 3.80-3.90 ppm signals appeared in the MLN resin spectrum, which indicates the presence of $-\text{CH}_2\text{OH}$ groups coming from the methylation reaction. This group could promote greater crosslinking of MLN resin during the curing reaction.

The resins' ^1H NMR spectra did not reveal the complexity of the chemical structure of these polymers, due to the overlapping of signals (Fig. 4). The ^{13}C NMR technique, in general, allows identification of a greater number of functional groups. Lignin-novolac spectra have a great many signals due to presence of lignin functional groups, which have a very complex structure. ^{13}C NMR spectra give an idea of the difficulty in understanding the resins structure, as shown in Fig. 5.

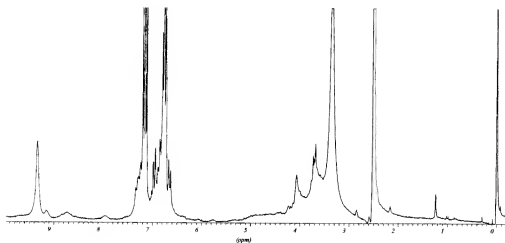


Figure 4 a. ^1H NMR spectrum of LN resin

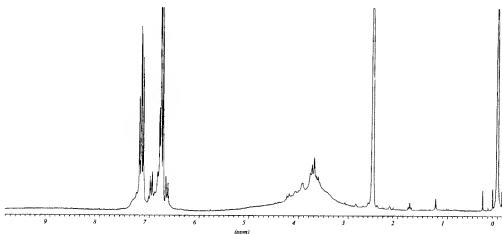


Figure 4 b. ^1H NMR spectrum of MLN resin

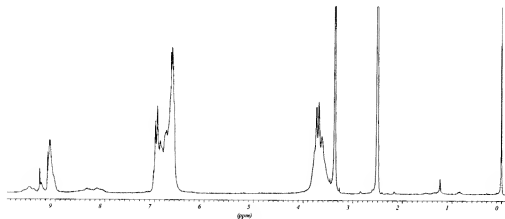


Figure 4 c. ^1H NMR spectrum of commercial novolac resins

An absence of peaks at 170-180 ppm implies that the aliphatic carboxylic acids were not formed in any of the three resins studied, which could make the resin curing reactions more difficult. The 166.5 ppm peak, which appears in the MLN spectrum, corresponds to the C=O link. This feature was also observed in the FTIR spectrum (Fig. 3.b), and it can be assigned to ester group linked to aromatic ring. The spectrum of commercial resin showed a signal at 150 ppm corresponding to OH linked to aromatic carbon, and this signal was unsubstituted in the *ortho* position by a CH_2 in LN and MLN. The same happens around 130 ppm, which is also a typical signal of novolac resins, due to C3 and C5 carbons of the phenolic ring substituted in its *ortho* position by a CH_2 (Holopainen et al. 1997). This signal, in novolac resins, is masked by resonances coming from lignosulfonate incorporated during polymer synthesis. The zone of 60-80 ppm (α , β and γ carbons of the (β)-aliphatic-O-(4)-aromatic links) was present only in the lignin-substituted resins. This range is consistent with the presence of a lignin structure. The zone of 35 ppm, characteristic of phenolic resins, is due to CH_2 in an *ortho* position with respect to the hydroxymethyl carbon group of phenolic ring (Holopainen et al. 1997).

Note that the incorporation of methylolated lignin instead of lignosulfonate presents a reaction mechanism similar to that shown in Fig. 2, with the exception that the formaldehyde cannot occupy *meta* sites in an aromatic ring. Although both mechanisms are similar in lignin samples, methylolated lignin presents methylene groups which will react with the phenol, while lignosulfonate (without modification) competes with methylene links between phenolic rings.

Summary of Results

Summarizing, despite a great number of signals and unavoidable overlapping, it was possible to distinguish novolac's typical signals by means of the three techniques employed. Identification of these signals implies that the lignin-novolac and methylolated lignin-novolac resins had similar links relative to commercial resin; however, resins synthesized with lignin showed a more complicated structure, due to lignin incorporation. Thus, LN and MLN would substitute for commercial resins in textile felt applications.

In the future an extensive characterization would be needed to determine and optimize cure process conditions for these polymers. In addition, other tasks should include evaluation of curing agent content (HMTA) during the cure process of the resins. Processing knowledge and kinetic methods developed for epoxy and unsaturated polyester resins should also benefit the manufacture of similar systems based on different polymers (Kenny et al. 1995; Boey et al. 2000; Lee et al. 2000).

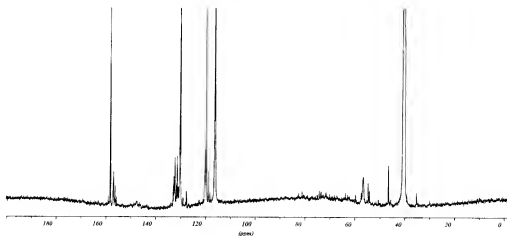


Figure 5 a. ¹³C NMR spectrum of LN resin

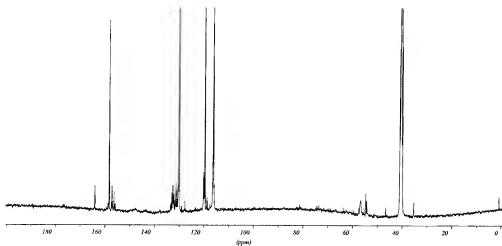


Figure 5 b. ¹³C NMR spectra of MLN resin

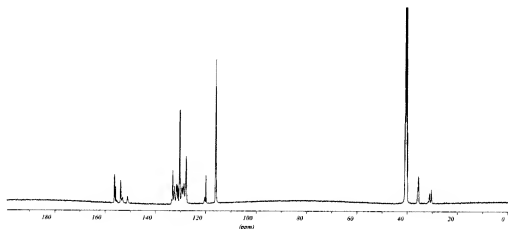


Figure 5 c. ^{13}C NMR spectra of commercial novolac resin

CONCLUSIONS

1. Phenol, formaldehyde, and water contents, as well as softening point and flow distance values of LN and MLN resins synthesized were in range with specifications that have been established for use of commercial novolac resins. Therefore, these samples conform to the specifications required for the textile felt applications.
2. FTIR and NMR spectroscopies showed that the chemical structure of lignin-novolac and methylolated lignin-novolac resins were more complicated than that of a commercial novolac resin due to the functional groups of the incorporated ammonium lignosulfonate.
3. Although the LN and MLN resins are structurally complex, the high variety of functional groups in relation to commercial resin could favour the curing reaction.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of "Ministerio de Ciencia y Tecnología" (project CTQ2004-02031/PPQ).

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Article submitted: March 19, 2006; First round of reviewing completed: April 12, 2007;
Revised version received May 5, 2007; Corrected version approved: May 23, 2007;
Article published May 25, 2007.